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Crystal structure of seven-membered acetals with furan and pyridine planar fragments

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Abstract

X-ray structure investigation of fused seven-membered acetals based on vitamin B_6 and 3,4-bis(hydroximethyl)furan have been performed. Molecules adopt chair conformations with equatorial position of substituents at acetal carbons; the geometry of acetal cycles resembles that of related seven-membered phthalylacetals. Stereochemistry of the tetracyclic adduct of furan-containing acetal with maleic anhydride was also investigated. The product exhibits endo–exo configuration with appreciably distorted seven-membered chair-like conformation.

Keywords: Fused heterocycles; Seven-membered acetals; Furan and vitamin B_6 derivatives; X-ray crystallography

1. Introduction

Seven-membered cyclic acetals with a planar fragment (1,3-dioxacyclohept-5-ene and its derivatives) provide examples on the coexistence of chair and twist-boat forms in solutions [1–12]. Conformational equilibrium position depends on the volume of alkyl or aryl substituents at the acetal carbon atom and the type of the planar fragment [2,8]. The Taft postulate was drawn on the series of conformationally inhomogeneous 2-R-1,3-dioxacyclohept-5-enes [13] in bromination [14] and [4 + 2]-cycloaddition reactions [15,16]. The data obtained provide the convincing evidence that chemical behavior is governed to a large extent by the stereochemical features of both chair and twist-boat structures, the bulkiness of substituents at C^2, electronic ability of the latter and finally substrate solvation. Contrary to what is usually observed in chair-like six-membered saturated carbo- and heterocycles, flexible 2-R-1,3-dioxacyclohept-5-enes can serve as suitable substrates for thorough understanding of the conformer's reactivity [13]. Our long lasting interest in chemistry of cyclic acetals prompted us to study seven-membered fused acetales with incorporation of heteroaromatic planar fragments. Attention was drawn to the systems containing furan (**I**) and pyridine (**II**)—moieties (in the latter cases vitamin B_6 derivatives). As to furan containing molecules the choice of these systems was motivated by wide application of such heterocycles in synthetic chemistry [17–19].

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